

Group-IV graphene- and graphane-like nanosheets

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Abstract

We performed a first principles investigation on the structural and electronic properties of group-IV (C, SiC, Si, Ge, and Sn) graphene-like sheets in flat and buckled configurations and the respective hydrogenated or fluorinated graphane-like ones. The analysis on the energetics, associated with the formation of those structures, showed that fluorinated graphane-like sheets are very stable, and should be easily synthesized in laboratory. We also studied the changes on the properties of the graphene-like sheets, as result of hydrogenation or fluorination. The interatomic distances in those graphane-like sheets are consistent with the respective crystalline ones, a property that may facilitate integration of those sheets within three-dimensional nanodevices.

Introduction

The properties of graphene, the one-atom-thick sheet with carbon atoms with the sp^2 hybridization, were first discussed in the literature more than sixty years ago.¹ It has been long considered only a theoretical curiosity of impossible experimental realization. This perception changed radically a few years ago, after the separation of graphene sheets with single and multiple layers.²⁻⁴

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Since then, graphene has been intensively investigated, with focus on its physical and chemical properties.⁵ This material carries unique properties that allows to envision a number of potential applications, such as chemical sensors,^{6,7} nanoelectronic devices,⁸ or hydrogen storage systems.⁹

Graphene could be considered as a prototypical material to study the properties of other two-dimensional nanosystems. Recently, several two-dimensional structures have been explored in the literature. For example, graphane, a fully hydrogenated graphene sheet with all carbon atoms in the sp^3 hybridization, has been proposed by theoretical investigations¹⁰ and was later synthesized.¹¹ Graphene-like sheets, made of silicon carbide,^{12,13} silicon,^{14,15} germanium,^{16,17} boron nitride,^{18,19} and zinc oxide²⁰ have also been discussed in the literature.

Here, we performed a systematic investigation on the trends in the properties of group-IV (C, SiC, Si, Ge, and Sn) graphene-like structures, in flat and buckled configurations, using first principles total energy calculations. We then observed the modifications on those properties as result of full coverage of hydrogen and fluorine atoms, to form sp^3 graphane-like structures. We found that hydrogenation and fluorination processes provide structures that were energetically very accessible for all compounds, and should be easily synthesized in laboratory. We also found that all group-IV graphene-like structures present null gaps in both flat or buckled configurations, that opened up with hydrogenation or fluorination in most materials. The only exception was the fluorinated graphane-like tin, that although tin atoms were fourfold coordinated, the material presented a null gap. This paper is organized as follow, we first discuss the methodology, then the properties of group-IV graphene-like sheets. Finally, we discuss the energetics and resulting physical properties of hydrogenated and fluorinated graphane-like sheets.

Methodology

The calculations were performed using the Vienna *ab initio* simulation package (VASP).²¹ The electronic exchange-correlation potential was described within the density functional theory and the generalized gradient approximation (DFT-GGA).²² The electronic wave-functions were de-

scribed by a projector augmented wave (PAW) method,²³ taking a plane-wave basis set with an energy cutoff of 550 eV. For all calculations, convergence in total energy was set to 0.1 meV/atom between two self-consistent iterations. Configurational optimization was performed by considering relaxation in all atoms, without symmetry constraints, until forces were lower than 3 meV/Å in any atom. The Brillouin zone was sampled by a $15 \times 15 \times 1$ Monkhorst-Pack k-point grid.²⁴ The planar structures were built using periodic boundary conditions with a hexagonal simulation cell. In the direction perpendicular to the sheets (z), we used a lattice parameter of 20 Å, which was large enough to prevent image interactions.

Binding and formation energies for all systems were computed following the same procedure presented elsewhere.¹⁰ The binding energy (E_B) of a certain structure was computed as the difference between the total energy of that stable structure and the total energies of the respective isolated atoms in their neutral charge states. The formation energy (E_F) of a certain hydrogenated (or fluorinated) sheet was computed as the difference between the binding energy of the graphane-like structure and the binding energies of the respective (stable) graphene-like structure and those energies of the diatomic molecules H_2 (or F_2). In group-IV materials, we found that the stable graphene-like structure was the buckled configuration (lower in energy), except for carbon.

The total energies of the isolated atoms and diatomic molecules were obtained considering a large simulation cell and the same methodological approximations of all the other calculations described in the previous paragraphs.

To check the validity of all approximations used in this investigation, we compared the properties of graphene with available data from experiments and other theoretical investigations. The computed binding energy of graphene was -7.848 eV/atom, being 0.136 eV/atom lower than the respective energy of the diamond cubic structure. Those two values are in excellent agreement with other investigations.^{25,26} In terms of the structural properties of graphene, the carbon-carbon interatomic distance was 1.425 Å, which is in excellent agreement with the respective experimental values (1.42 Å),¹ but a little larger than the one (1.414 Å) of a recent theoretical investigation.¹⁵ It should be pointed out that while our investigation used a generalized gradient approximation

the other investigation used the local density approximation, that is known to underestimate interatomic distances.¹⁵

Results

Figure 1 presents a schematic representation of the graphene-like structures in flat (labeled α) and buckled (labeled β) configurations and their hydrogenated and fluorinated graphane-like forms. Table 1 presents the structural properties of group-IV graphene-like sheets and their respective binding energies. According to the table, the graphene-like structures of Si, Ge and Sn in flat (α) configurations are metastable, with the respective buckled ones (β) being energetically more favorable, consistent with other investigations for Si.^{15,16}

Figure 2 presents the theoretical interatomic distances and binding energies of all group-IV graphene-like and graphane-like structures as function of the respective properties in the (diamond cubic or zinc-blende) crystalline solid phases, in which all group-IV atoms are in the sp^3 hybridization.²⁷ According to Figure 2a, interatomic distances between group-IV atoms in flat graphene-like structures are on average 5 % shorter than those distances in the respective solid phases. These results show that the group-IV atoms, in a sp^2 environment, behave essentially the same way as carbon atoms do. For the buckled configurations, those distances are always larger than the respective ones in the flat configurations. Buckling distances (Δz) are consistent with recent theoretical results for buckled sheets of silicon and germanium.¹⁶

Figure 2b shows that the binding energies of most group-IV graphene-like structures in either flat or buckled configurations, except for carbon, are higher than the respective energies in the solid phases. This indicates that graphene-like structures, with atoms in the sp^2 hybridization, are not very stable when compared to the respective solid stable phases, in which atoms are in the sp^3 hybridization. These results are consistent with the generally large energy difference between those two hybridizations in most covalent materials, being small only for carbon. Additionally, the binding energy in the buckled configurations is larger than the one in the flat configurations,

except for carbon. In the case of carbon, the calculations indicated that the buckled configuration is unstable, relaxing toward the flat one. An interesting case is SiC, in which the binding energy difference between flat and buckled configurations is only 1 meV/atom, but the buckling is also small. All those graphene-like structures, in either flat or buckled configurations, presented a null electronic gap, except for SiC, that presented a large gap of 2.54 eV. This value is in excellent agreement with a recent theoretical investigation using similar approximations.^{12,13}

Figure 3 presents the electronic band structure of all graphene-like structures in flat and buckled configurations. All group-IV graphene-like structures (of C, Si, Ge, and Sn) in a flat configuration (fig. 3a) present a similar electronic band structure, with a band crossing in the Dirac (K) points at the Fermi level. For all of those materials, there is linear dispersion around those Dirac points, a property that results from the honeycomb structure. In buckled configurations (Fig. 3b), the linear dispersion around those Dirac points is maintained.

The electronic band structures of the flat graphene-like configurations differ among themselves only by the fact that, in structures of C and Si, the system is semi-metallic, being metallic in Ge and Sn ones. Such difference in the band structure could be understood by the following explanation. For graphene-like flat structures of C and Si, there is a specific energy band that stays over the Fermi level in all the Brillouin zone. However, for graphene-like flat structures of Ge and Sn, the same band crosses the Fermi level in the $\Gamma \rightarrow M$ symmetry direction, and the system is metallic. The electronic band structure of the flat and buckled configurations differ by the fact that the later ones do not present the band crossing described in this paragraph.

Since the electronic band structure of group-IV graphene-like materials, in flat configurations, are equivalent to the one of carbon, we computed the carrier velocities around their respective Dirac points. From the results of Figure 3, the computed carrier velocities in those points are 0.91, 0.58, 0.59, and 0.52×10^6 m/s for flat graphene-like of C, Si, Ge, and Sn, respectively. The computed carrier velocities in those points are 0.46, 0.69, and 0.95×10^6 m/s for buckled graphene-like of Si, Ge, and Sn, respectively. Those results indicate that carrier velocities around the Dirac points could be very large in the buckled configurations. Our result for graphene is in good agreement with the

experimental value of 1.1×10^6 m/s (Refs.² and²⁸) and with the theoretical one of 0.63×10^6 m/s (Ref.¹⁵).

1 presents the structural parameters for hydrogenated and fluorinated graphane-like structures and their respective binding and formation energies. Here, we considered only systems associated with the chair-like configurations, and neglected the boat-like isomeric ones. This is justified by recent theoretical investigations for graphane^{10,29} and fluorinated graphane,³⁰ indicating that the chair-like configuration is energetically more favorable than the boat-like one. As described in Figure 1c (or 1d), the chair-like configuration has hydrogen (or fluorine) atoms alternating over and below the plane containing the group-IV atoms. Incorporation of either hydrogen or fluorine atoms leads to very stable structures, with binding energies (per atom) for graphane-like structures larger than the ones for graphene-like, as shown in Figure 2b. Additionally, the graphane-like structures have large formation energies in most cases, consistent with other theoretical investigations for hydrogen incorporation in graphene¹⁰ and in boron nitride graphene-like structures.¹⁸

Figure 2b shows the trends in the binding energies (per atom) for hydrogenated and fluorinated graphane-like structures. The fluorinated structures are energetically more stable than the hydrogenated ones, and become considerably favorable for Si, Ge, and Sn materials. These results are consistent with available experimental results for graphane and fluorinated graphane structures.^{11,29} Therefore, it is expected that those fluorinated graphane-like forms should be easily synthesized in laboratory.

In terms of the structural properties of hydrogenated and fluorinated forms, 1 presents the interatomic and buckling distances. The interatomic distances between the group-IV atoms and hydrogen (or fluorine) atoms are in excellent agreement with the respective distances in typical organic molecules. For example, in graphane (C_2H_2) the C-C, C-H, and buckling (Δz) distances are 1.536, 1.110, and 0.459 Å agree very well with recent theoretical results¹⁵ of 1.520, 1.084, and 0.45 Å, respectively. For fluorinated graphane-like structure (C_2F_2), the C-C and C-F distances are 1.583 and 1.382 Å that agree well with recent theoretical results²⁹ of 1.579 and 1.371 Å, respectively. According to Figure 2a, along the series, interatomic distances between group-IV

atoms, in either hydrogenated or fluorinated forms, are all very close to the interatomic distances in their respective crystalline forms.

The results indicate that group-IV atoms, in hydrogenated and fluorinated graphane-like structures, are fourfold coordinated and have a near tetrahedral configuration, and their interatomic distances and binding are close to the ones in a crystalline environment. The structures deviated from a tetrahedral configuration, evidenced by the buckling distance (Δz), due to some ionic character in the binding between the group-IV atoms and the hydrogen (or fluorine) neighboring atoms. The results suggest that hydrogenation or fluorination may generate two-dimensional structures that could be easily incorporated in the surface of the respective three-dimensional crystalline counterparts. Therefore, while integration of graphene-like structures in three-dimensional devices is still difficult, due to large lattice mismatch, it may be easier for hydrogenated and fluorinated graphane-like structures.

According to Figures 3c and 3d, hydrogenation and fluorination open the electronic gap of the graphene-like structures. In all cases, electronic gap is larger in the hydrogenated configurations than in the fluorinated ones. An interesting case is the fluorinated graphane-like tin (Sn_2F_2), in which although tin atoms have a fourfold coordination, the material has a null gap. This result indicates that carrier velocities should be very large in this system, even with tin atoms with all valence electrons paired with neighboring atoms.

Summary

In summary, we investigated the trends on the structural and electronic properties of graphene-like structures made of group-IV atoms, in terms of their energetics and electronic band structure. The results indicate that while the graphene-like structures (of Si, Ge, Sn, and SiC) appear to have low stability, the respective hydrogenated and fluorinated graphane-like ones are very stable and should be easily synthesized in laboratory.

The hydrogenated and fluorinated graphane-like structures present the group-IV atoms in a

fourfold configuration and in a near tetrahedral configuration. Interatomic distances in those configurations are close to the respective ones in the solid phase counterparts, a property that could facilitate integration of those two-dimensional structures within three-dimensional nanodevices.

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Table 1: Structural and electronic properties of graphene-like sheets (α -XY and β -XY respectively for flat and buckled sheets) and hydrogenated (XYH₂) or fluorinated (XYF₂) graphane-like sheets with X = Y = C, Si, Ge, or Sn (or X = C and Y = Si for SiC). The table presents the lattice parameter (a), interatomic distances (d), buckling distances (Δz), binding (E_B), formation (E_F), and electronic bandgap (E_g) energies. Interatomic distances, binding and formation energies, and electronic bandgap energies are given respectively in Å, eV/atom, and eV.

	a	$d(X-Y)$	$d(X-H)$	$d(X-F)$	$d(Y-H)$	$d(Y-F)$	Δz	E_B	E_F	E_g
α -C ₂	2.468	1.425					0	-7.848		0.0
C ₂ H ₂	2.539	1.536	1.110				0.459	-5.161	-0.111	3.47
C ₂ F ₂	2.609	1.583		1.382			0.488	-5.403	-0.802	3.10
α -Si ₂	3.897	2.250					0	-3.894		0.0
β -Si ₂	3.867	2.279					0.459	-3.914		0.0
Si ₂ H ₂	3.968	2.392	1.502				0.687	-3.379	-0.297	2.11
Si ₂ F ₂	3.968	2.395		1.634			0.697	-4.656	-2.019	0.70
α -Ge ₂	4.127	2.383					0	-3.114		0.0
β -Ge ₂	4.061	2.444					0.690	-3.243		0.0
Ge ₂ H ₂	4.091	2.473	1.563				0.730	-2.882	0.107	0.95
Ge ₂ F ₂	4.182	2.492		1.790			0.617	-3.892	-1.349	0.19
α -Sn ₂	4.798	2.770					0	-2.581		0.0
β -Sn ₂	4.639	2.841					0.947	-2.728		0.0
Sn ₂ H ₂	4.719	2.846	1.738				0.824	-2.517	-0.030	0.45
Sn ₂ F ₂	5.028	2.951		1.970			0.531	-3.625	-1.581	0.0
α -SiC	3.100	1.790					0	-5.905		2.54
β -SiC	3.098	1.788					0.001	-5.906		2.54
SiCH ₂	3.124	1.892	1.108		1.497		0.573	-4.366	-0.288	4.04
SiCF ₂	3.168	1.914		1.445		1.609	0.563	-5.096	-1.463	1.94

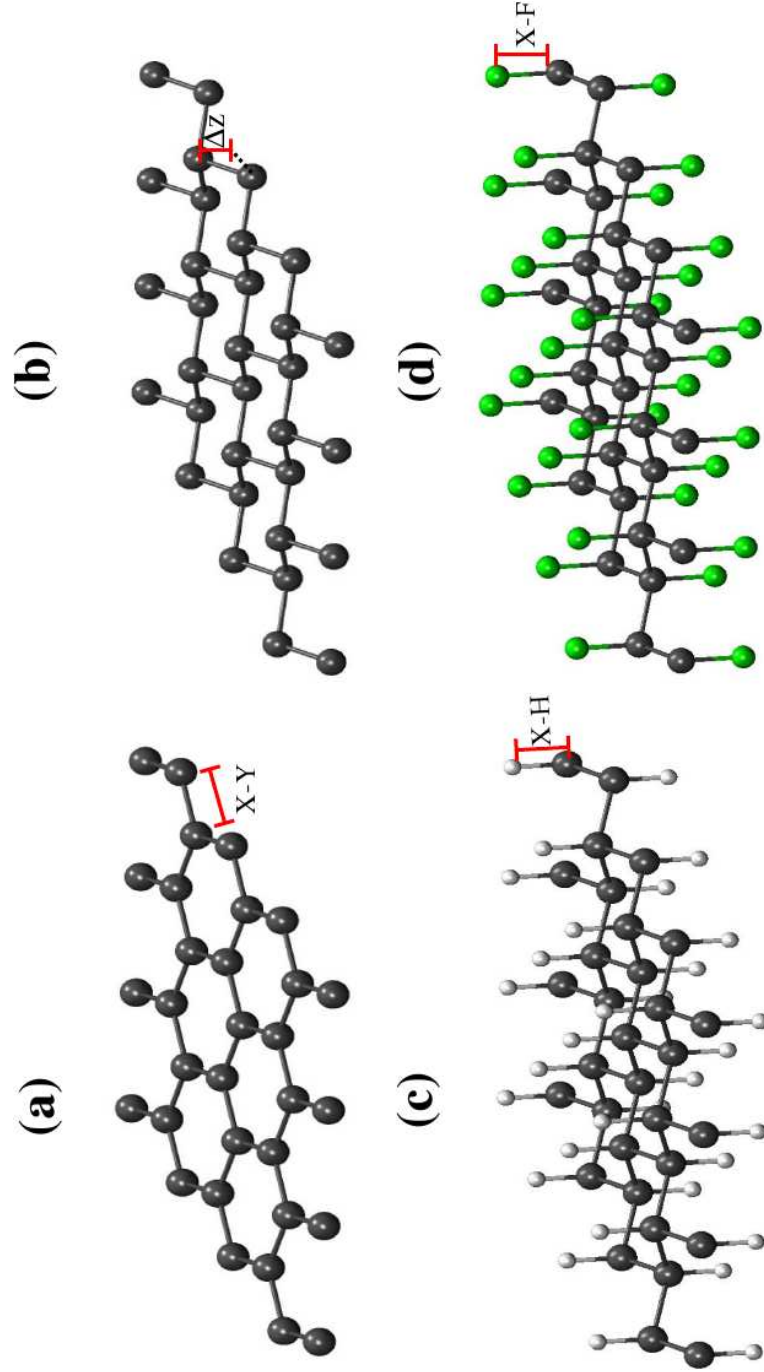


Figure 1: (color online) Schematic representation of group-IV two dimensional materials: (a) flat graphene-like (α), (b) buckled graphene-like (β), (c) hydrogenated graphane-like, and (d) fluorinated graphane-like structures. The figure also indicate the interatomic distance labels, consistent with the ones in 1. Black, grey and green spheres represent group-IV, hydrogen and fluorine atoms, respectively.

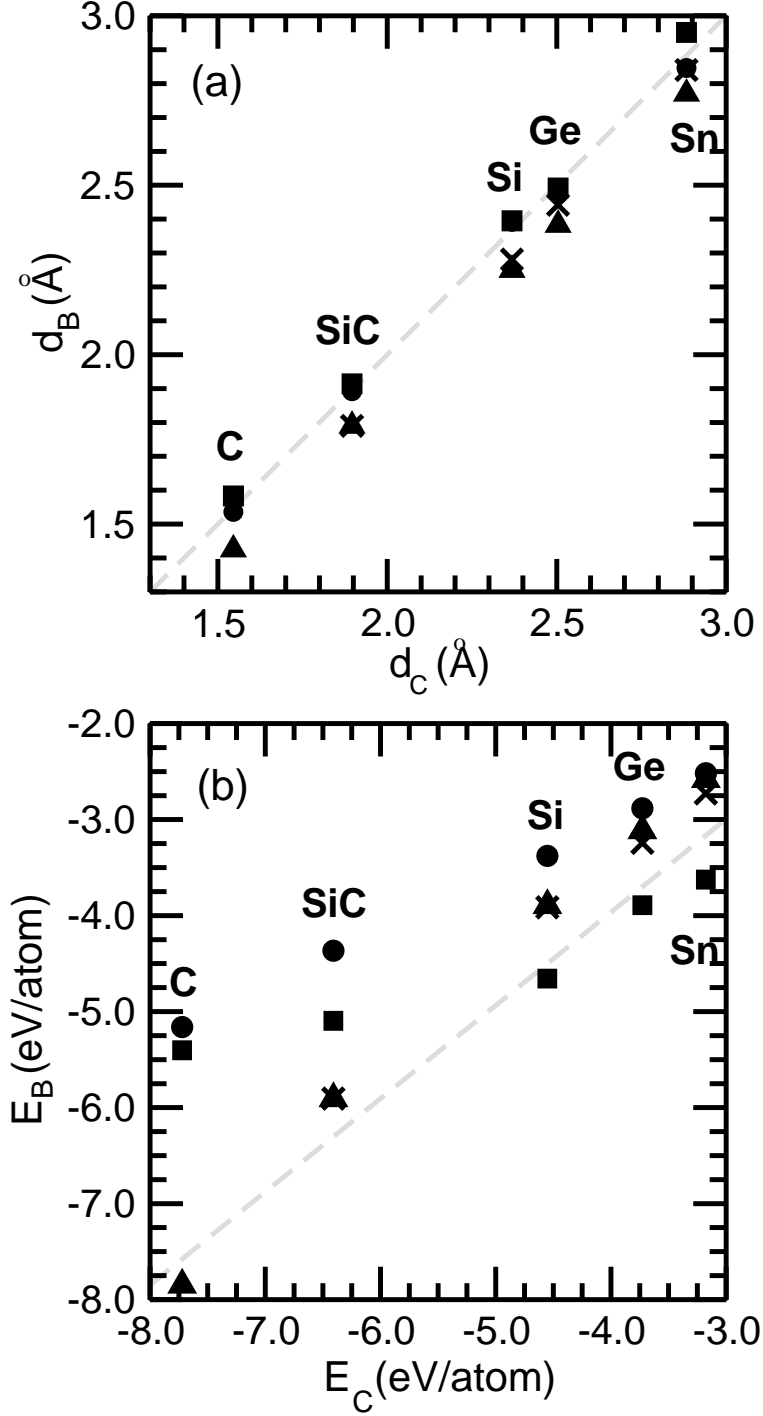


Figure 2: Properties of group-IV (C, SiC, Si, Ge, and Sn) graphene-like (in flat and buckled sheets) and graphane-like structures (with full coverage of H or F atoms). The figure shows the (a) interatomic distances (d_B) and (b) binding energies (E_B) of those structures as function of the respective distances (d_C) and binding energies (E_C) in the diamond cubic (or zinc-blende) crystalline structures. The \blacktriangle , \times , \bullet , and \blacksquare symbols represent respectively the flat graphene-like (α), buckled graphene-like (β), hydrogenated graphane-like, and fluorinated graphane-like structures. The dashed lines are only a guide to the eye, representing the properties $d_B = d_C$ in (a) and $E_B = E_C$ in (b).

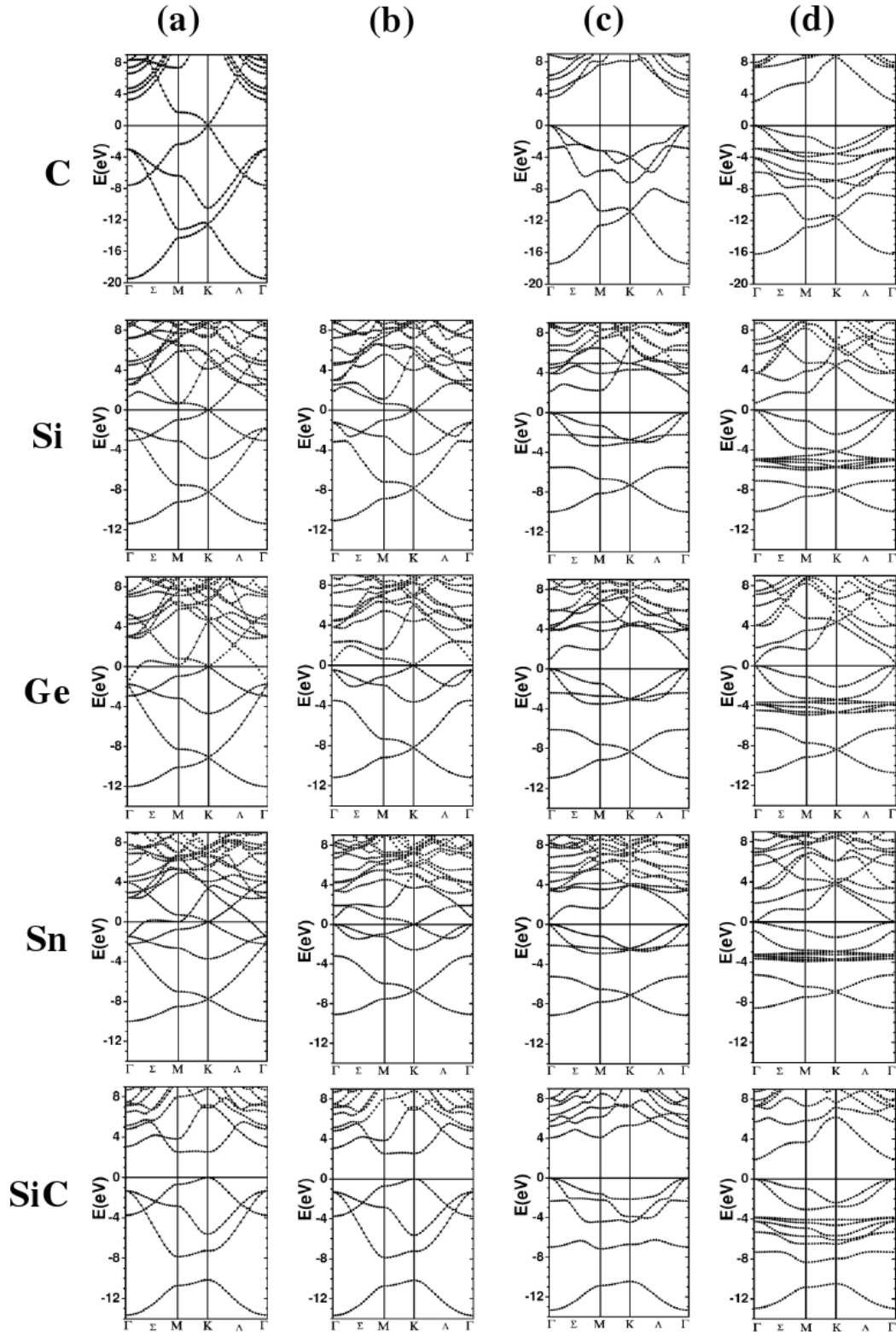


Figure 3: Electronic band structure of group-IV in (a) flat graphene-like (α), (b) buckled graphene-like (β), (c) hydrogenated graphene-like, and (d) fluorinated graphene-like structures.